

# Disorder-Induced First Order Transition and Curie Temperature Lowering in Ferromagnetic Manganites.

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We study the effect that size disorder in the cations surrounding manganese ions has on the magnetic properties of manganites. This disorder is mimicked with a proper distribution of spatially disordered Manganese energies. Both, the Curie temperature and the order of the transition are strongly affected by disorder. For moderate disorder the Curie temperature decreases linearly with the variance of the distribution of the manganese site energies, and for a disorder comparable to that present in real materials the transition becomes first order. Our results provide a theoretical framework to understand disorder effects on the magnetic behavior of manganites.

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Compounds with chemical formula  $R_{1-x}A_x\text{MnO}_3$  ( $R$ =trivalent element and  $A$ =divalent element) are usually called manganites. These materials exhibit an extraordinarily large (so called colossal) magnetoresistance. The study of the origin of the colossal magnetoresistance as well as its possible technological applications has triggered in the last years an intensive research on these materials[1, 2, 3]. This research has revealed a rich variety of exotic phenomena, and after twenty years of intense study new and exciting phenomena still appear when studying manganites[4, 5, 6, 7].

In manganites the ferromagnetic order is driven by the motion of the carriers and, therefore, their properties depend on the competition between kinetic energy, tending to delocalize the carriers, and localization effects, such as antiferromagnetic coupling between the Mn core spins and the Jahn-Teller coupling. Disorder also reduces the carriers mobility, and, thus, it strongly affects the stability of the ferromagnetic (FM) phases. Recently it has been possible to synthesize cation ordered  $\text{Ln}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ , where Ln is a rare earth and LnO and BaO planes alternate along the  $c$  axis[8]. These half-doped manganites may give a good benchmark to test theories of the influence of disorder on the electronic and magnetic properties of manganites. Experimental work in FM  $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$  shows[9] that disorder strongly suppresses the transition temperature and changes the character of the transition, from continuous to weakly first order.

Attfield and coworkers[10, 11] found that in FM perovskites of the form  $\text{AMnO}_3$ , the variation of Curie temperature with disorder is related with the distribution of the A cations radius,  $r_A$ , and there is not significant dependence on the A site charge variance. Therefore, we expect that the observed[9] difference in  $T_c$  between the ordered and disordered  $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$  perovskites is related with the different distributions of  $r_A$ . Note that standard ionic radii values are  $r_A = 1.21$  for  $\text{La}^{3+}$  and  $r_A = 1.47$  for  $\text{Ba}^{2+}$ [11]. In the ordered  $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$  perovskite, Fig.1(a), alternating planes of LaO and BaO separate  $\text{MnO}_2$  sheets in such a way that each Mn ion

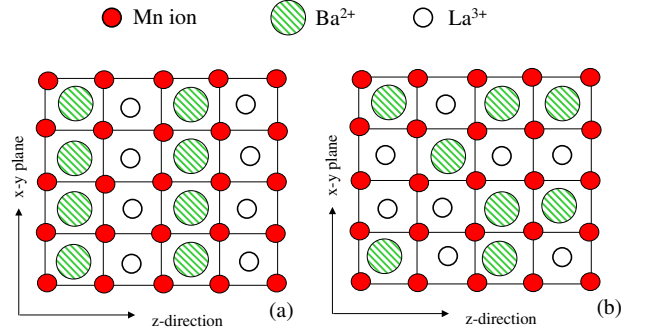


FIG. 1: (color online) Schematic representation of an ordered (a) and disordered (b)  $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$  perovskite. In the ordered case planes containing La and Ba cations alternate along the  $z$ -direction. In the disorder case the cations are randomly distributed.

has four  $\text{La}^{3+}$  neighbors in a direction and four  $\text{Ba}^{2+}$  neighbors in the opposite direction being all the Mn ions equivalent. In the disorder perovskites, Fig.1(b), the La and Ba cations are randomly distributed and the Mn's are surrounded by different combinations of divalent and trivalent cations. These different chemical environments translate in different *chemical pressures* on the Mn ions, and is a source of disorder in the Mn electronic levels.

In this work we combine Ginzburg-Landau formalism with realistic two orbital DE microscopic calculations, to study the effect that the disorder in the position of the trivalent and divalent cations has on the magnetic properties of FM manganites. The main results of the work are, i) The Curie temperature,  $T_c$  decreases with the disorder, ii) as the disorder increases, the FM-PM phase transition becomes more abrupt and eventually, for a critical disorder, the magnetic transition becomes first order and iii) we identify the variance of disorder distribution as the relevant parameter for the decrease of  $T_c$ . All these three points agree with the experimental

results[9, 11, 12]. Our analytical results provide a framework for understanding the dependence of  $T_c$  on disorder, both, in experiments and in Monte Carlo simulations of simplified models[13, 14, 15, 16].

*Model.* In a manganite of formula  $R_{1-x}A_x\text{MnO}_3$ , there are  $4-x$  electrons per Mn ion. The crystal field splits the Mn  $d$  levels into an occupied strongly localized  $t_{2g}$  triplet and a doublet of  $e_g$  symmetry. Furthermore, the Hund's coupling in Mn ions is very large and aligns the spins of the  $d$  orbitals. Effectively, there are  $1-x$  electrons per Mn ions hopping between the empty  $e_g$  Mn states.

The large Hund's coupling forces each electron spin to align locally with the core spin texture. The spin of the carriers is conserved in the hopping between Mn ions, being the tunnelling amplitude maximum and the kinetic energy minimum, when the spins of the Mn ions are parallel and the system is ferromagnetic. This is basically the so called double exchange (DE) mechanism proposed fifty years ago by Zener[17] to explain the FM order in manganites. When the temperature increases the kinetic energy minimized by the FM order competes with the orientational entropy of the Mn core spin and at  $T_c$ , the system becomes paramagnetic (PM)[18]. In the PM phase the reduction of the kinetic energy could favor that localization effects become more effective and a metal insulator transition could occur near the FM-PM transition[19]. In the case of  $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ , the localization effects are rather weak and the material is metallic at both sides of the FM-PM transition. Therefore, in our model we do not consider coupling with the lattice, however as the DE mechanism depends strongly in the kinetic energy gain, we treat the motion of the carriers in a realistic way by including the two  $e_g$  orbitals.

*Hamiltonian.* With the above considerations, the two orbital DE Hamiltonian takes the following form,

$$H = \sum_{\langle i,j \rangle, a, b} f_{i,j} t_{a,b}^u C_{i,a}^+ C_{j,b} \sum_{i,a} \epsilon_i \hat{n}_{i,a} , \quad (1)$$

here  $C_{i,a}^+$  creates an electron in the Mn ion located at site  $i$  in the  $e_g$  orbital  $a$  ( $a=1,2$   $1=|x^2-y^2\rangle$  and  $2=|3z^2-r^2\rangle$ ). In the limit of infinite Hund's coupling, the spin of the carrier should be parallel to the Mn core spin  $\mathbf{S}_i$ , and the tunnelling amplitude is modulated by the spin reduction factor

$$f_{i,j} = \cos \frac{\vartheta_i}{2} \cos \frac{\vartheta_j}{2} + e^{i(\phi_i - \phi_j)} \sin \frac{\vartheta_i}{2} \sin \frac{\vartheta_j}{2} \quad (2)$$

where  $\{\vartheta_i, \phi_i\}$  are the Euler angles of the Mn core spins. The hopping amplitude depends both on the direction  $u$  between sites  $i$  and  $j$  and the orbitals involved;  $t_{1,1}^{x(y)} = \pm\sqrt{3}t_{1,2}^{x(y)} = \pm\sqrt{3}t_{2,1}^{x(y)} = 3t_{2,2}^{x(y)} = t$ . In the  $z$  direction the only nonzero term is  $t_{2,2}^z = 4/3t$  [1]. Hereafter  $t$  is taken as the energy unit.

The last term describes the diagonal disorder.  $\hat{n}_{i,a} = C_{i,a}^+ C_{i,a}$  is the occupation operator of orbital  $a$  at site  $i$  and  $\epsilon_i$  is the energy shift produced by the *chemical pressure* on the Mn ion at site  $i$ . This shift affects equally

both  $e_g$  orbitals. As discussed above, the *chemical pressure* at site  $i$  depends on the ionic radii of the cations surrounding the Mn ion. We assume that the total shift at site  $i$  is the sum of the shifts produced by the eight next neighbors cations. Cations with big ionic radius induce a positive energy shift  $\Delta$  whereas cations with small ionic radius induce a negative energy shift  $-\Delta$ . With this election a Mn ion surrounded by equal number of small and large cations has zero energy shift. In the case of a manganite of composition  $\text{R}_{0.5}\text{A}_{0.5}\text{MnO}_3$  the diagonal shift takes values in the range  $-8\Delta < \epsilon_i < 8\Delta$ . In this description of the cationic disorder the strength of the disorder is defined by the value of  $\Delta$ .

*Free energy.* In order to describe thermal effects we have to compute the free energy. In manganites the Fermi energy of the carriers is much greater than the typical Curie temperature and we only consider the entropy of the classical Mn core spins. In the mean field approximation[20] and in the limit of small magnetization, the entropy per Mn core spin takes the form,

$$S(m) = \frac{\log 2}{2} - \frac{3}{2}m^2 - \frac{9}{20}m^4 + \dots \quad (3)$$

where  $m$  is the thermal average of the relative magnetization of the Mn core spins.

At finite temperatures the magnetization is not saturated and the spin reduction factor, Eq. (2) is smaller than unity. Treating the spin fluctuations in the virtual crystal approximation, the spin reduction factor is substituted by its expectation value, that for small magnetization has the form[21],

$$f_{i,j} \simeq f_m = \frac{2}{3} - \frac{2}{5}m^2 - \frac{6}{175}m^4 + \dots \quad (4)$$

With this the thermal average of the internal energy per Mn ion can be written in the form,

$$E = \frac{f_m}{N} \left( \sum t_{a,b}^u \langle C_{i,a}^+ C_{j,b} \rangle + \frac{1}{f_m} \sum \epsilon_i \langle \hat{n}_{i,a} \rangle \right) \quad (5)$$

being  $N$  the number of Mn ions in the system. In Eq. (5), it is evident that the relative importance of the disorder increases when the magnetization, and thus the spin reduction factor decreases. For small values of  $\Delta$  the internal energy can be expanded in powers of the disorder strength. As the mean value of  $\epsilon_i$  is zero, the first term different from zero is proportional to the variance,  $\sigma^2(\epsilon_i)$ , of the diagonal disorder distribution,

$$E = f_m \left( E_0 + a \frac{\sigma^2(\epsilon_i)}{f_m^2} \right) , \quad (6)$$

where  $E_0 < 0$  is the kinetic energy per Mn ions in the disorder free FM phase, and

$$\sigma^2(\epsilon_i) = \frac{1}{N} \sum_i \epsilon_i^2 . \quad (7)$$

In Eq. (6), the coefficient  $a$  is negative as the electrons prefer to place on sites with negative values of  $\epsilon_i$ .

Combining Eq. (3-7), the dependence of the free energy,  $F = E - TS$ , on the magnetization, can be written as

$$F = \frac{3}{2}Tm^2 + \frac{2}{5}\left(E_0 - \frac{9}{4}a\sigma^2(\epsilon_i)\right)m^2 + \frac{9}{20}Tm^4 - \frac{6}{175}\left(E_0 - \frac{39}{2}a\sigma^2(\epsilon_i)\right)m^4 + \dots \quad (8)$$

and the Curie temperature takes the form

$$T_c = -\frac{4}{15}\left(E_0 - \frac{9}{4}a\sigma^2(\epsilon_i)\right), \quad (9)$$

where is clear that  $T_c$  decreases when the disorder strength increases. The order of the transition can be inferred from the sign of the quartic term in Eq. (8). If the quartic term is positive the transition is second order, while a negative quartic term implies the existence of a first order phase transition. Using the previous expression for  $T_c$ , a first order transition takes place if,

$$\sigma^2(\epsilon_i) > \frac{2}{39}\frac{E_0}{a}\left(\frac{1+\frac{7}{2}}{1+\frac{21}{52}}\right). \quad (10)$$

Equations (9) and (10) are the main results of this work, they show that the Curie temperature decreases when the strength of the disorder increases and that for disorder strong enough the FM-PM transition changes from second to first order. Comparing Eq. (9) and Eq.(10) it results that for changes in the Curie temperature larger than 10 per cent, the FM-PM transition transforms from second to first order.

*Numerical results.* In order to check the approximations we have done and the validity of the obtained results, we diagonalize numerically the ferromagnetic two orbital DE Hamiltonian, in presence of diagonal disorder, Eq. (1). We consider the case of disorder in the ionic radii of the cations surrounding the Mn ions. As discussed above, this disorder produces a distribution of diagonal energy shifts in the range  $-8\Delta < \epsilon_i < 8\Delta$ . For a random distribution of the two type of cations, the variance of the diagonal disorder distribution is  $\sigma^2(\epsilon_i) = 8\Delta^2$ . We have diagonalized the Hamiltonian for different disorder realization and different values of the disorder strength  $\Delta$ . We work with a cluster containing  $12 \times 12 \times 12$  atoms and with periodic boundary conditions. By studying smaller clusters we have checked that our results are free of finite size effects.

In Fig.2a we plot, for the full polarized FM phase, the internal energy per Mn ion as function of the disorder strength  $\Delta$ . As expected[22], for small values of the disorder the internal energy decreases quadratically with  $\Delta$ . Taking into account the dependence of the internal energy on the spin reduction factor, in mean field approximation the Curie temperature gets the form

$$T_c = -\frac{2}{3}\frac{\partial U}{\partial m^2}. \quad (11)$$

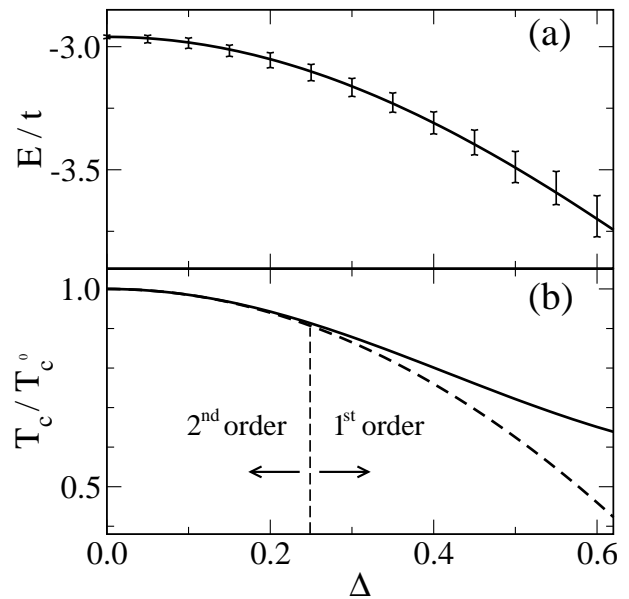


FIG. 2: Polynomial fit to a) internal energy and b) Curie temperature as obtained from numerical simulations. Bars in a) indicates the typical indetermination in the numerical calculations. In b) the dashed line corresponds to the quadratic approximation to  $T_c$  (Eq. (9)). In b) the regions with first and second order FM-PM transition are shown.

In Fig.2b, we plot  $T_c$ , as obtained numerically from the internal energy, as function of  $\Delta$ . In the disorder free case,  $T_c \sim 0.8t$  that compared with the Curie temperature of the ordered  $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ ,  $T_c=350\text{K}$ , [9], implies a value of the hopping amplitude of  $t \sim 0.038\text{eV}$ . For changes up to 20 per cent, we find that the decrease of  $T_c$  with  $\Delta$  can be fitted very accurately with a quadratic dependence. Experimentally the differences in  $T_c$  between the ordered and disordered samples in  $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$  is near 14 per cent[9], therefore we expect that for manganites with atomic radii size disorder, the expressions obtained analytically for  $T_c$ , Eq. (9), and the order of the transition, Eq. (10) should be valid.

In fig.2b, we also indicate the disorder strength for which the magnetic transition changes from second to first order. As discussed above, the transition becomes first order for changes in  $T_c$  larger than 10 per cent. In the case of  $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ , the disorder produces changes in  $T_c$  of near 14 per cent and therefore our results explain the experimentally observed change in the order of the magnetic transition[9]. We expect that in FM manganites with smaller differences in the atomic radii than in  $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ , for example  $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  ( $r_A = 1.21$  for  $\text{La}^{3+}$  and  $r_A = 1.31$  for  $\text{Sr}^{2+}$ [11]) the effect of the disorder in  $T_c$  should be smaller and the order of the magnetic transition should be second order independently of the order in the position of the cations.

Finally we want to check that, as proposed by Rodríguez-Martínez and Attfield[11], the relevant figure for quantifying the disorder is the variance of the disorder

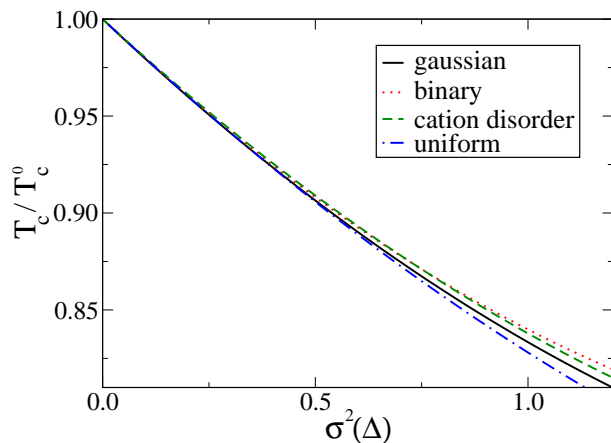


FIG. 3: (*color online*) Curie temperature versus variance of diagonal disorder for different models of disorder. The different kinds of disorder are explained in the text

distribution. We have repeated the numerical calculation of  $T_c$  for different distribution of diagonal disorder. Apart from the *cation disorder* distribution, we have also analyzed a *uniform* distribution of the diagonal energy shift between two values, a *binary* distribution and a *gaussian* distribution of the diagonal disorder.

The results are plotted in Fig.3. For all models studied, we find that for moderate disorder strength, the Curie temperature decreases linearly with the variance of the disorder. There are deviations from this depen-

dence in the limit of strong disorder. In this limit the carriers start to localize in the sites with smaller energy and perturbation theory becomes not valid. This regime is not the relevant one in FM manganites, and the results shown in Fig. 3 agree with the experimental results obtained by Rodríguez-Martínez and Attfield[11]. The numerical results also support our analytic findings that for moderate disorder strength the variation of the Curie temperature and the order of the transition depend on the variance of the distribution of the diagonal energy shifts in the electronic Hamiltonian.

In summary, we have studied a realistic model of manganites by means of exact microscopic calculations and Landau Theory formalism. The different sizes of cations surrounding a manganese ion are included in the model as an energy shift in that manganese site. This model reproduces the experimental results. It explains the observed strong reduction of  $T_c$  in disordered samples with respect to ordered ones[9]. Moreover, it demonstrates, in agreement with experiments[9], that disorder makes the FM-PM transition more abrupt and, for a enough disorder strength, this transition becomes first order. Finally our formalism identifies in a natural way the variance of the distribution of the diagonal energy shifts, as the relevant parameter to characterize changes in the magnetic properties, independently of the model of disorder[11, 12, 23].

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